Biogeosciences, 11, 7275–7289, 2014
www.biogeosciences.net/11/7275/2014/
doi:10.5194/bg-11-7275-2014


Biogeosciences Open Access

# Spring bloom community change modifies carbon pathways and C : N : P : Chl *a* stoichiometry of coastal material fluxes

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Received: 3 June 2014 – Published in Biogeosciences Discuss.: 6 August 2014
Revised: 6 November 2014 – Accepted: 22 November 2014 – Published: 19 December 2014

**Abstract.** Diatoms and dinoflagellates are major bloom-forming phytoplankton groups competing for resources in the oceans and coastal seas. Recent evidence suggests that their competition is significantly affected by climatic factors under ongoing change, modifying especially the conditions for cold-water, spring bloom communities in temperate and Arctic regions. We investigated the effects of phytoplankton community composition on spring bloom carbon flows and nutrient stoichiometry in multiyear mesocosm experiments. Comparison of differing communities showed that community structure significantly affected C accumulation parameters, with highest particulate organic carbon (POC) buildup and dissolved organic carbon (DOC) release in diatom-dominated communities. In terms of inorganic nutrient drawdown and bloom accumulation phase, the dominating groups behaved as functional surrogates. Dominance patterns, however, significantly affected C : N : P : Chl *a* ratios over the whole bloom event: when diatoms were dominant, these ratios increased compared to dinoflagellate dominance or mixed communities. Diatom-dominated communities sequestered carbon up to 3.6-fold higher than the expectation based on the Redfield ratio, and 2-fold higher compared to dinoflagellate dominance. To our knowledge, this is the first experimental report of consequences of climatically driven shifts in phytoplankton dominance patterns for carbon sequestration and related biogeochemical cycles in coastal seas. Our results also highlight the need for remote sensing technologies with taxonomical resolution, as the C : Chl *a* ratio was strongly dependent on community composition and bloom stage. Climate-driven changes in phytoplankton dominance patterns will have far-reaching consequences for major biogeochemical cycles and need to be considered in climate change scenarios for marine systems.

## 1 Introduction

Coastal seas and shelf areas (< 200 m deep) constitute approximately 5 % of the ocean but are among the most vital marine biotopes, both from an ecological and from a socioeconomical perspective. They connect terrestrial, atmospheric, and marine biogeochemical cycles, and it has been estimated that ∼ 12 % of the marine primary production and ∼ 86 % of the total carbon burial in the ocean takes place in coastal regions (Dunne et al., 2007). Coastal seas also play a pivotal role in trophic transfer of organic carbon from primary producers through the food web, and they include some of the richest fisheries in the world. At the same time, these areas are the most affected by direct and indirect anthropogenic pressures and are highly vulnerable to projected global change (Halpern et al., 2008). Multiple drivers of the marine food web – such as temperature, UV irradiation, $pCO_2$, and runoff of nutrients and freshwater – are affecting the ecosystem on different levels. One of the key issues for predicting how global change will affect coastal marine environments is to identify population dynamics and feedback loops under a changing environment (Harley et al., 2006; Eggers et al., 2014).

Temperate aquatic systems are characterized by high productivity, especially of new production, as opposed to recycled production (Dugdale and Goering, 1967). Their production is highly seasonal, and the annual spring bloom

represents the most significant production phase. High initial concentrations of inorganic nutrients, increasing solar radiation, and emerging stratification of water layers trigger the onset of photosynthetic production. Several bloom-forming phytoplankton groups compete for resources in marine environments during spring, the most conspicuous being diatoms, dinoflagellates, and prymnesiophytes. Recent evidence from both coastal and offshore environments shows decadal shifts in the relative proportions of diatoms and dinoflagellates at different seasons and suggests that their competition is significantly affected by climatic factors under ongoing change (Leterme et al., 2005; Hinder et al., 2012), modifying especially the spring bloom conditions of temperate and Arctic regions. Mild winters and more storms have been shown to favor dinoflagellates (Klais et al., 2013), and also changes in thermal stratification patterns and freshwater runoff are thought to affect phytoplankton community composition; for example diatoms typically dominate during times with high turbulence, whereas dinoflagellates are more common after firm stratification has been established (Smayda and Reynolds, 2001). The extensive temperate and Arctic shelf seas and marginal ice zones are globally among the most susceptible biotopes for climate change, and their changing production preconditions will potentially have a great impact on global carbon budgets and interconnected biogeochemical cycles. The consequences of climate-driven phytoplankton community change represent therefore urgent challenges for reliable climate change scenarios.

The physiology and morphology of different phytoplankton species and groups vary considerably, with direct impacts on ecosystem-wide nutrient cycling and cascading food web effects. Differences in species-specific traits like growth rate, nutrient affinities and biochemical composition, cell size, motility, and life cycle strategies govern the outcome of resource competition, and therefore the community composition in a set of environmental conditions. They also directly affect system-level carbon sequestration, stoichiometry of material flows, and the export of organic carbon to the sea floor. Several of these functional aspects of algal physiology are thus relevant for large-scale biogeochemical cycles, and their incorporation in trait-based models of phytoplankton production (Litchman and Klausmeier, 2008; Litchman et al., 2010) would significantly enhance the predictive potential of marine biogeochemical models under climate change.

Among the temperate coastal seas projected to change most rapidly is the Baltic Sea, due to its close interaction with the intensively modified catchment, the predicted changes in annual precipitation patterns over northern Europe, its reduced alkalinity, and heavy fishing pressure (Niiranen et al., 2013). In the Baltic Sea, cold-water dinoflagellates and diatoms have been considered functional surrogates during the spring bloom, as both effectively deplete the wintertime inorganic nutrient concentrations (Tamminen, 1995; Kremp et al., 2008), and the bloom terminates in most basins once nitrate has been consumed below analytical detection limits (Tamminen and Andersen, 2007). However, there are obvious differences with respect to life cycle strategies and sedimentation patterns of the competing phytoplankton groups. In general, diatoms sink quickly to the sea floor once nutrients are depleted, and it has been shown that the fraction of the population forming resting spores is highly species-specific (Rynearson et al., 2013). Dinoflagellates, on the other hand, lyse before reaching the sediment, or alternatively go through a life cycle transformation producing decomposition-resistant resting cysts (Heiskanen, 1998).

The differences in sedimentation patterns have a large impact on decomposition of the bloom biomass in sediments, with consequences on oxygen consumption and release of phosphorus (Spilling and Lindström, 2008); this should also affect the decomposition by pelagic bacteria. This indicates strong cascading effects of bloom community composition on benthic food webs and material cycles. Although grazing pressure is relatively low during the spring bloom period in the Baltic Sea (Lignell et al., 1993), phytoplankton species composition has been shown to affect also the planktonic grazer communities because of species-specific differences in food quality for the emerging copepod populations (Vehmaa et al., 2011). Therefore, the cascading effects of bloom composition are potentially pervasive within the whole ecosystem.

In this study, we investigate the effects of phytoplankton community composition on stoichiometry of planktonic biogeochemical processes, in a coastal model system displaying ongoing, climate-driven community change (the Baltic Sea; Klais et al., 2011). We hypothesize that a change in phytoplankton community composition (here, diatom vs. dinoflagellate dominance) will significantly modify the carbon budget and stoichiometric composition of the seston. The data originate from coastal mesocosm experiments with nutrient enrichments performed in 5 consecutive years, with multiweek time series of phytoplankton species composition, primary production, and nutrient fractions in a total of 36 mesocosms. The experiments displayed natural phytoplankton communities of interannually highly variable relative contributions of diatoms and cold-water dinoflagellates ($< 10$ to $> 90$ % of either group) to the total bloom biomass.

## 2 Materials and methods

### 2.1 Experimental setup

The mesocosm experiments were conducted in spring 2004 to 2008 under laboratory conditions at the Tvärminne Zoological Station, University of Helsinki. The experimental setup consisted of a control unit of natural seawater and three nutrient manipulation treatments: a combined nitrate (N) and phosphate (P) addition; a dissolved silicate (DSi) addition; and a combined N, P, and DSi addition. On top of the nutrient manipulations, different treatments were added. In

**Table 1.** Summary of the experimental setup in different years. The treatments were nutrient addition (NPSi), which were additions of nitrogen (N), phosphorus (P), and silicate (Si) in N–P, Si and N–P–Si additions. The light treatment (light) was a low- and high-light treatment, 20 and 90 µmol photons $m^{-2}$ $s^{-1}$, respectively. In 2005 there was only the nutrient addition treatment and in 2007 there cultured diatoms were added in a gradient (diatom gradient). The diatoms added were *Thalassiosira levanderi* (∼ 10 µm diameter and was added to a final concentration of 20 000, 75 000 and 13 350 cells $L^{-1}$) and *T. baltica* (20–30 µm diameter and was added to a final concentration of 2000, 3560 and 13 350 cells $L^{-1}$), two very typical spring bloom species. The start concentration of $NO_3$ (Start $NO_3$) gives the concentration in µg $L^{-1}$ of $NO_3$ in the control and in the treatments with N addition. The peak Chl *a* values are the minimum and maximum concentration recorded in the control (no nutrient addition) and in treatments with nutrients added, respectively.

| Year | Start date | Duration days | Treatments | Start $NO_3$ µg $L^{-1}$ | Start Chl *a* µg $L^{-1}$ | Peak Chl *a* µg $L^{-1}$ |
|---|---|---|---|---|---|---|
| 2004 | 24 Mar | 44 | NPSi, light | 90/260 | 7.1 | 21/78 |
| 2005 | 7 Apr | 28 | NPSi | 100/250 | 2.9 | 20/184 |
| 2006 | 19 Apr | 23 | NPSi, light | 8/170 | 35.0 | 39/199 |
| 2007 | 16 Mar | 33 | NPSi, diatom gradient | 90/250 | 4.9 | 22/77 |
| 2008 | 12 Mar | 28 | NPSi, light | 100/280 | 0.6 | 43/70 |

2004, 2006, and 2008, two different light environments were used, in a full factorial $2^3$ design; in 2005, only the nutrient treatments were used; in 2007, two cultured diatoms typical for the spring bloom in the area – *Thalassiosira levanderi* (∼ 10 µm diameter) and *T. baltica* (20–30 µm diameter) – were added in a gradient to the natural communities. The final concentration of *T. levanderi* was 20 000, 75 000, and 21 2000 cells $L^{-1}$; the final concentration of *T. baltica* was 2000, 3560, and 13 350 cells $L^{-1}$. A summary of the experimental design and initial conditions in the experimental units is given in Table 1.

For each experiment, containers were filled with natural surface water and pre-screened with a 200 µm mesh-size net to remove metazooplankton. Water was collected during ice breakup from the ice edge near the Storfjärden monitoring station at the SW coast of Finland (59°51′ N; 23°13′ E). In 2004, white plastic (PE) 80 L barrels were used as experimental units, whereas, for the years 2005 to 2008, 25 L transparent polycarbonate carboys were used.

Ice breakup typically coincides with the initiation of the annual spring bloom in the area (Niemi, 1975), and the captured phytoplankton community was assumed to represent the seed community for the spring bloom. The timing of ice breakup varied between years, and accordingly the experiments were started on different dates in subsequent years, depending on the ice situation.

After filling containers on the ice, they were immediately brought to the laboratory; the water was divided into mesocosm carboys and placed into a walk-in incubator set to 2 °C. The mesocosms were illuminated by daylight-spectrum, fluorescent tubes (Philips TLD-95) at a 12 h light–12 h dark cycle, corresponding to the ambient light cycle. Different irradiance was used for different treatments (Table 1). Prefiltered (0.2 µm) air was bubbled into the mesocosms to keep a low level of turbulence.

Natural nutrient conditions were manipulated by additions of $NO_3-N$, $PO_4-P$ (N+P treatment), and/or $SiO_2-Si$ (DSi treatment), with similar nutrient manipulations carried out each year. Nutrient additions (see Table 1 for the initial $NO_3$ concentrations) were targeted at approximately doubling the typical wintertime concentrations in the area, while maintaining a balanced Redfield ratio (a molar N : P ratio of 16). Irradiance was adjusted to 20 µmol photons $m^{-2}$ $s^{-1}$ for the low-light treatment (LL), which was applied in the 2004, 2006, and 2008 experiments and to 90 µmol photons $m^{-2}$ $s^{-1}$ for the high-light treatment (HL). In 2005 and 2007, all treatments received 90 µmol photons $m^{-2}$ $s^{-1}$.

The successive years represented different initial conditions, due to differences in ice breakup and other meteorological history of the winter–early spring season. The ambient nutrient concentrations of each experiment thus represented varying phases of the early bloom period despite similar experimental additions, between full wintertime levels and the spring depletion period. The initial, natural phytoplankton community varied from year to year.

### 2.2 Sampling protocol and measurements

Mesocosms were sampled for Chlorophyll *a* (Chl *a*), nutrients and phytoplankton immediately after the addition of nutrients on day 0, and subsequently every 2 to 3 days. The duration of the experiment differed between years, depending on how fast nutrients were exhausted (Table 1). Prior to sampling, which took place at the beginning of the daily light period; the contents of the mesocosms were stirred with a polycarbonate rod to ensure an even distribution of phytoplankton and other particulate matter. The samples thus represent bloom development without sedimentation losses. The total sampling volume never exceeded half the total volume.

Samples for dissolved and particulate nutrients and Chl *a* were processed immediately. Nutrient concentrations ($NO_3-N$, $PO_4-P$, and DSi) were determined manually in duplicate from each carboy according to the standard colorimetric methods (Grasshoff et al., 1983). Dissolved organic

carbon (DOC) concentrations were measured by the high-temperature catalytic oxidation (HTCO) method using a Shimadzu TOC-V CPH carbon and nitrogen analyzer. Subsamples (< 0.45 µm Supor Acrodisc PES filter, Gelman Sciences) were acidified to pH 2.5 with 2 M HCl and stored in darkness at room temperature. The 20 mL glass ampoules were stored for 4 to 6 months, before determining the DOC concentration according to Sharp et al. (1993).

For the determination of Chl *a*, 50 mL duplicate samples from each carboy were filtered onto glass-fiber filters (Whatman GF/F) and extracted in 10 mL of 94 % ethanol for 24 h in the dark at room temperature. Chl *a* was measured on a Shimadzu RFPC-5001 fluorometer, calibrated with pure Chl *a* (Sigma). Duplicate filters (50–100 mL filtered depending on the biomass concentration) were also prepared for determination of particular organic carbon (POC), nitrogen (PON), and phosphorus (POP). For all samples acid-washed, precombusted GF/F filters were used. The filters were allowed to dry and stored at room temperature (20 °C) until nutrient determination. POC and PON were measured from the same filter with a mass spectrometer (Europa Scientific). POP was determined according to Solórzano and Sharp (1980).

Phytoplankton samples were preserved with acid Lugol's solution. Prior to microscopic analysis, volumes of 50 and 25 mL were set up for concentration in Utermöhl chambers and allowed to settle for at least 24 h. Diatoms and dinoflagellates, identified to species or genus level, were counted with an inverted light microscope (Leica DM IRB, Wetzlar, Germany). Cells were grouped into two size categories (> and < 10 µm), which were counted separately at ×200 and ×787 magnification. At least half of the chamber bottom was screened when cell densities were low; otherwise 400 cells were counted, if possible, for each category. Cell dimensions of diatoms and dinoflagellates were measured on 25 randomly selected cells of each species, and biovolumes were calculated using formulas given for standard geometric shapes of phytoplankton taxa (Sun and Liu, 2003). Biovolume values were converted to carbon according to the recommendations of Menden-Deuer and Lessard (2000).

Radiolabeled $^{14}C$ was used to determine the total primary production, and this was determined on all sampling days. An activity of 0.15 kBq was added to 10 mL of sample and incubations carried out in the same light and temperature conditions as for the mesocosms. After an incubation period of 3 h, a 4 mL sample was extracted, 150 µL of 37 % formaldehyde was added to fix the sample, and 100 µL of 1 M HCl was added in ventilation cupboard to remove unassimilated (inorganic) $^{14}C$ isotope. The samples were left with the lid open for 24 h before 7 mL of liquid scintillation cocktail (Hi Safe) was added. The radioactivity was measured using a liquid scintillation counter (PerkinElmer Inc., Wallac Winspectral 1414). The amount of total dissolved inorganic carbon (DIC) was measured with a high-temperature combustion infrared (IR) carbon analyzer (Unicarbo, Electro Dynamo, Finland). Primary production was calculated from uptake of $^{14}C$ knowing the total amount of added isotope and total DIC. Due to the relatively short incubation period, measured primary production was assumed to represent gross primary production (Sakshaug et al., 1997).

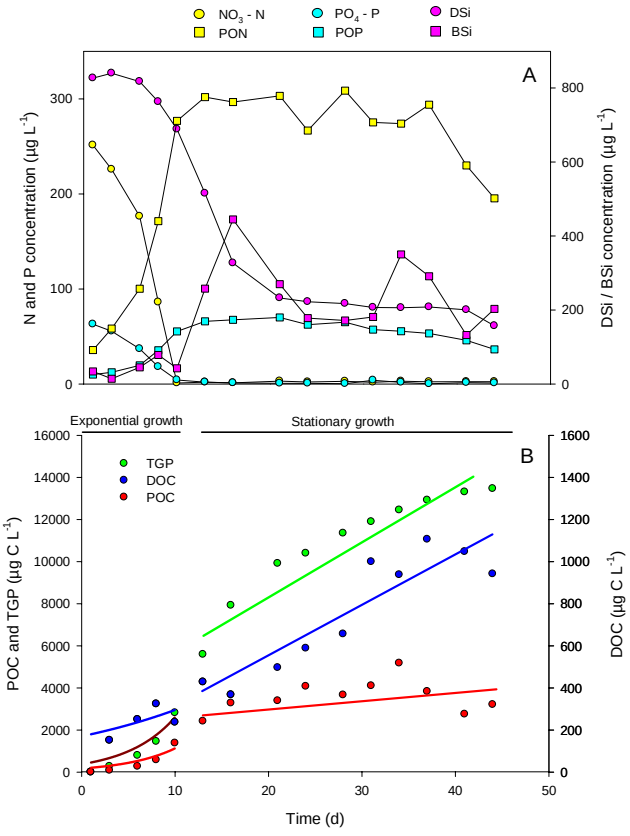


**Figure 1.** An example of the data extracted from the mesocosms (data from high-light treatment with N and P addition, 2004): dissolved, inorganic nutrients and particulate, organic nutrients **(a)** and carbon parameters **(b)**. The parameters are nitrate ($NO_3$), particulate organic nitrogen (PON), phosphate ($PO_4$), particulate organic phosphorus (POP), dissolved silicate (DSi), biogenic silicate (BSi), particulate organic carbon (POC), dissolved organic carbon (DOC), and total gross production (TGP). All parameters were measured directly except TGP, which was extrapolated from short-term $^{14}C$ incubations. The growth was divided into exponential and stationary growth phases based on the primary production peak ($L^{-1}$), indicated with the horizontal bars on top **(b)**. Note the different scales on the *y* axes.

## 2.3 Data treatment

The development of dissolved inorganic nutrients and POC, PON, POP, Chl *a*, and DOC were organized as a function of time (e.g., Fig. 1). Background levels of refractory DOC are very high in the Baltic Sea – e.g., 350–400 µmol C $L^{-1}$ as DOC in the open Gulf of Finland (Hoikkala, 2012) – so the start concentration was subtracted from all values to express DOC change during the experiment. The

phytoplanktondevelopment was divided into two growth stages: exponential and stationary growth phase. The exponential growth phase was defined from the start of the experiment until the primary production peak per volume (i.e., not normalized to biomass); stationary growth phase was defined as the period after this point until the end of the experiment.

The community growth rate ($\mu$) was determined during the exponential growth phase for the biomass-related parameters ($\mu_{POC}$, $\mu_{Chla}$) by linear regression of the natural log transformed data. The exponential growth of DOC ($\chi_{DOC}$) was done in the same way. During stationary growth phase a linear regression (without log transformation) was fitted to the data parameters in order to find the rate of change.

Primary production was modeled from the $^{14}C$ incubations, assuming the measured production to represent the whole light period ($12\,h\,d^{-1}$). Sampling did not take place every day, and we estimated the carbon fixation between sampling days by linear regression. A simple model was created, summing the gross carbon fixation for each day, and this was termed total gross production (TGP). This accumulated gross primary production would be the theoretical development of POC without any loss processes.

The growth rate of TGP ($\mu_{TGP}$) was calculated similarly to the other biomass-related parameters described above, and carbon assimilation efficiency (CAE) was calculated from the ratio between the measured carbon accumulation and total gross production:

$$CAE = \mu_{POC}/\mu_{TGP}. \quad (1)$$

Carbon loss rate (CLR) was calculated as the fraction of TGP not entering the POC pool:

$$CLR = 1 - CAE. \quad (2)$$

Respiration (RES) was calculated as the part of the loss rate not released as DOC, assuming that all carbon not adding to the POC or DOC pools was used for respiration.

$$RES = CLR - (\chi_{DOC}/\mu_{TGP}) \quad (3)$$

The CAE, CLR, and RES parameters were also calculated for the stationary growth phases, with the difference that the rate of change were used instead of growth rate, e.g., $\Delta_{POC}$ instead of $\mu_{POC}$.

Phytoplankton community composition data were used for calculating the proportion of dinoflagellates and diatoms of the total community biomass. Species evenness (Shannon's equitability, $H_E$) was calculated as follows:

$$H_E = -[p_i \cdot \ln(p_i/S)], \quad (4)$$

where $p_i$ is the proportion of $i$th species biovolume from total biovolume of the sample, and $S$ is the number of species present in the sample.

ANOVA on ranks were used to check for statistical significance ($\alpha = 0.05$) between different phytoplankton community composition for the different carbon budget parameters.

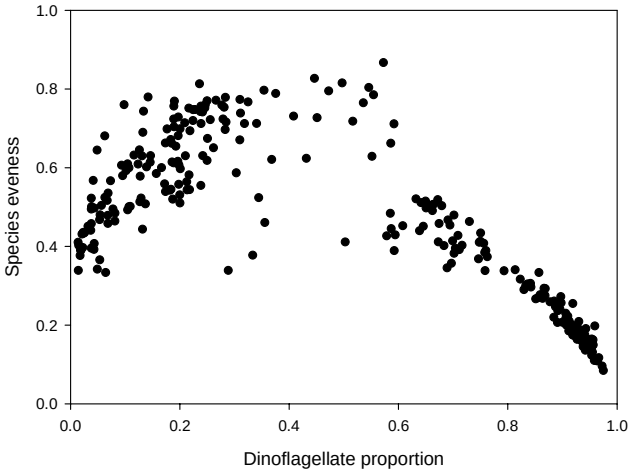


**Figure 2.** Species evenness plotted against the dinoflagellate proportion of the whole community. For later analysis, the phytoplankton community was divided into three categories: diatom dominance (> 80 %), mixed community (20–70 % dinoflagellates), and dinoflagellate dominance (> 70 %). The rationale behind setting the group boundaries was based upon the apparent difference in species evenness.

"On ranks" were used because of a low normal distribution score for several parameters using the Anderson–Darling test ($A^2 > 1$ and $p < 0.05$). The ANOVA and regression analysis were carried out in SigmaPlot (SPSS).

## 3 Results

### 3.1 Phytoplankton community

The initial phytoplankton community composition varied from year to year, with relative proportions of the total biomass ranging from > 90 % diatoms to > 90 % dinoflagellates. In general, there were more species of diatoms present in the mesocosms compared to dinoflagellates. The most abundant diatoms were *Thalassiosira baltica*, *T. levanderi*, *Chaetoceros wighamii*, *Skeletonema marinoi*, and *Achnanthes taeniata*, and two dinoflagellates were dominating: *Biecheleria baltica* and *Peridiniella catenata*. Species evenness was highest in a mixed community, when dinoflagellates constituted 20–70 % (i.e., 30–80 % diatoms) of the total population (Fig. 2). The effect on evenness was less pronounced when diatoms dominated. During diatom dominance, several species were represented, whereas, during dinoflagellate dominance, only one out of the two species accounted for most of the biomass (*B. baltica* in 2004 and *P. catenata* in 2007). The phytoplankton community was divided into three categories: diatom dominance (> 80 %), mixed community (20–70 % dinoflagellates) and dinoflagellate dominance (> 70 %). The rationale behind setting the group boundaries

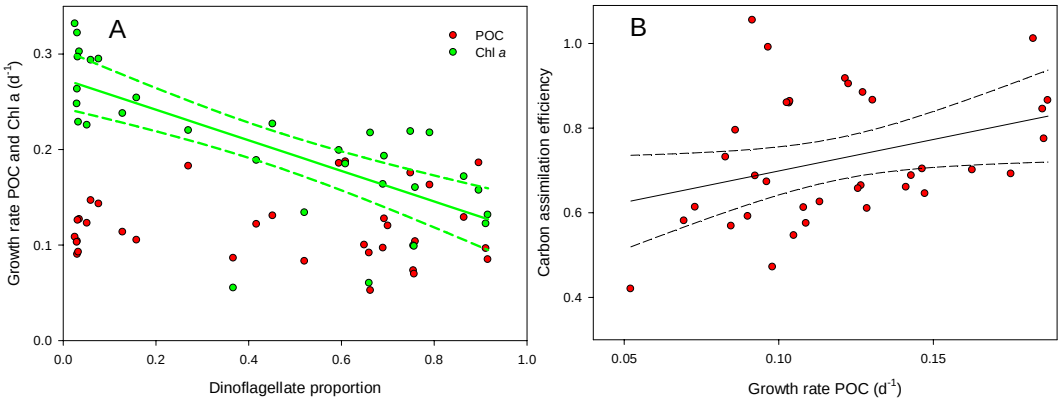


**Figure 3.** The growth rate during exponential growth of particulate organic carbon ($\mu_{POC}$) and Chlorophyll *a* ($\mu_{Chl\ a}$) at different dinoflagellate proportion of the total phytoplankton community **(a)**, and the relationship between carbon assimilation efficiency and $\mu_{POC}$ **(b)**. No significant trend was found for $\mu_{POC}$, but a negative correlation was found between $\mu_{Chl\ a}$ and dinoflagellate proportion. The solid line represents the linear regression (slope $= -0.16$; $R^2 = 0.53$; $p < 0.0001$), and the dashed lines represent the 95 % confidence intervals. The carbon assimilation efficiency is the ratio between the measured growth rate in POC and the total gross production (Fig. 1). A positive correlation was found (slope $= 1.49$; $R^2 = 0.12$; $p = 0.04$).

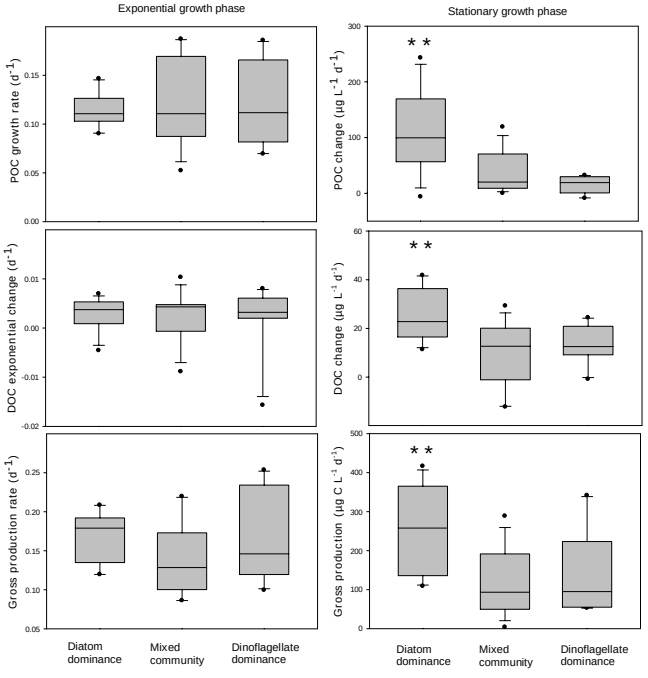


**Figure 4.** Carbon budget parameters: particulate organic carbon (POC), dissolved organic carbon (DOC), and total gross production, during exponential and stationary growth. The phytoplankton community was divided into three categories: diatom dominance (> 80 %), mixed community (20–70 % dinoflagellates), and dinoflagellate dominance (> 70 %). The rationale behind setting the group boundaries was based upon the apparent difference in species evenness (Fig. 2) between these groups. The stars (*) indicate statistical significance ($\alpha = 0.05$) against one (*) or two groups (**); details can be found in Tables 3 and 4.

was based upon the apparent difference in species evenness (Fig. 2).

The dominance of either diatoms or dinoflagellates was almost complete, being at > 90 % of the total phytoplankton biomass during the experiments, with the exception of 2008 (mixed community) when chrysophytes made up 10–20 % of the biomass.

### 3.2 Carbon budget

The community carbon growth rate ($\mu_{POC}$) was clearly affected by the light conditions, but not by the community composition. The average $\mu_{POC}$ under the low- and high-light conditions (20 and 90 µmol photons $m^{-2}\ s^{-1}$) were 0.08 ($d^{-1}$) $\pm$ 0.01 (SD) and 0.15 ($d^{-1}$) $\pm$ 0.02 (SD), respectively. There was no significant difference in $\mu_{POC}$ between different community compositions (Fig. 3a). However, the growth rate calculated from Chl *a* ($\mu_{Chl\ a}$) was highest in diatom-dominated communities and decreased linearly ($p < 0.0001$) with increasing dinoflagellate proportion (Fig. 3a). The carbon assimilation efficiency (CAE) was positively correlated ($p = 0.04$) with the growth rate (Fig. 3b).

During exponential growth, there was no apparent difference between phytoplankton communities in gross primary production (Fig. 4, Table 2). There was, however, an effect on the CAE and respiration (RES). The mixed community had on average a ~ 30 % higher CAE and ~ 75 % lower RES compared to the situations when dinoflagellates or diatoms dominated (Fig. 4, Tables 2 and 3).

In the stationary growth phase, the community composition clearly had an effect on the carbon budget (Fig. 4, Tables 2 and 4). When diatoms constituted > 80 % of the population, there was on average 3–7 times higher buildup of POC, ~ 2 fold higher TGP, and ~ 2-fold higher

**Table 2.** Statistical comparison using one-way ANOVA on ranks. Tukey's post hoc test of statistically significant differences (*) can be found in Table 3 (exponential growth phase) and 4 (stationary growth phase).

| Exponential growth phase | | | | | |
|---|---|---|---|---|---|
| Parameter | DF | SS | MS | $F$ value | $p$ value |
| POC | 2 | 5.58 | 2.79 | 0.026 | 0.974 |
| DOC | 2 | 29.3 | 14.6 | 0.140 | 0.870 |
| TGP | 2 | 313 | 156 | 1.637 | 0.211 |
| CAE | 2 | 888 | 444 | 5.770 | 0.007* |
| RES | 2 | 941 | 471 | 6.258 | 0.005* |
| Stationary growth phase | | | | | |
| POC | 2 | 1395 | 678 | 9.246 | $< 0.001$* |
| DOC | 2 | 958 | 479 | 5.399 | 0.009* |
| TGP | 2 | 1084 | 542 | 6.386 | 0.005* |
| CAE | 2 | 739 | 369 | 3.874 | 0.031* |
| RES | 2 | 564 | 282 | 2.804 | 0.075 |

release of DOC compared to the situations with mixed or dinoflagellate-dominated communities (Fig. 5, Tables 2 and 4). The diatoms also had the highest CAE during stationary growth but with no statistical difference with a mixed community (Table 4).

### 3.3 Stoichiometry

The phytoplankton community clearly affected the stoichiometry of the seston, with C : N and C : P ratio being higher during diatom dominance (Fig. 6). The drawdown of inorganic N and P was close to 100 % and stayed stable after the onset of stationary growth phase (e.g., Fig. 1a). There was a significant, negative correlation between C : N and C : P ratios with increasing dinoflagellate proportion during both exponential and stationary growth phase ($p \leq 0.03$). The C : N ratio was a factor of 1.2–1.7 times higher than the Redfield ratio during exponential growth phase, and it increased to 1.7–3.6 times higher than the Redfield ratio in all communities during stationary growth phase.

The C : P ratio was up to 1.4 times higher than the Redfield ratio during exponential growth in diatom-dominated communities; dinoflagellate-dominated communities were approximately on par with the Redfield ratio. During stationary growth phase the C : P ratio increased to 1.4–2.8 times higher than the Redfield ratio.

The N : P ratio for most samples fell below the Redfield ratio of 16 and did not vary between communities during exponential growth ($p = 0.23$). After nutrients had been depleted, however, there was a negative correlation of N : P ratio with increasing dinoflagellate proportion ($p < 0.001$) (Fig. 6).

The N : Si ratio was lowest during diatom dominance ($p < 0.001$) and increased with dinoflagellate dominance, especially during exponential growth phase (Fig. 6). In general,

**Table 3.** Tukey's post hoc tests of carbon parameters during exponential growth phase. Only the statistically significant parameters from Table 2 were tested: carbon assimilation efficiency (CAE) and respiration (RES). The phytoplankton community was categorized according to diatom dominance (diatoms), mixed community (mixed) and dinoflagellate dominance (dinoflagellates). The stars (*) indicate statistically significant differences ($\alpha = 0.05$).

| CAE | Diff | St diff | $p$ value |
|---|---|---|---|
| Mixed vs. diatoms | 10.833 | 3.026 | 0.013* |
| Mixed vs. dinoflagellates | 10.517 | 2.800 | 0.023* |
| Dinoflagellates vs. diatoms | 0.317 | 0.084 | 0.996 |
| RES | | | |
| Mixed vs. diatoms | 11.583 | 3.272 | 0.007* |
| Mixed vs. dinoflagellates | 10.183 | 2.743 | 0.026* |
| Dinoflagellates vs. diatoms | 1.400 | 0.377 | 0.925 |

the drawdown of N and P and buildup of biomass (e.g., POC) were very similar in the N, P and N, P & Si treatment and in the control and Si addition.

The C : Chl *a* ratio was clearly affected by the phytoplankton community composition and growth phase ($R^2 = 0.53$, $p < 0.0001$) (Figs. 3 and 7), and there was on average a trend of decreasing ratios during exponential growth followed by increasing ratios during stationary growth phase. At the start of the experiment, the average C : Chl *a* ratios (comparing only high-light treatments) were $477 \pm 338$ (SD), $84 \pm 51$ (SD), and $55 \pm 31$ (SD) gC (g Chl $a)^{-1}$ for diatom-dominated, mixed, and dinoflagellate-dominated communities, respectively. The initial decrease in the C : Chl *a* ratio was most rapid during diatom dominance ($95 \pm 74$ (SD) at the primary production peak), whereas there was less change for mixed communities and during dinoflagellate dominance ($60 \pm 60$ (SD) and $45 \pm 17$ (SD), respectively, at the primary production peak). The C : Chl *a* ratio started to increase again during the stationary growth phase and was, at the end of the experiment, $208 \pm 62$ (SD), $218 \pm 155$ (SD), and $387 \pm 49$ (SD) for diatom-dominated, mixed, and dinoflagellate-dominated communities, respectively.

## 4 Discussion

### 4.1 Natural mixed communities as an experimental system

Differences in the physiology and cellular composition of diatoms and dinoflagellates have been recurrently established in monocultures (Chan, 1980; Banse, 1982; Menden-Deuer and Lessard, 2000), with the general conclusion that diatoms show higher maximum growth rates, higher photosynthetic rates per unit carbon, and lower C : Chl *a* ratios compared to dinoflagellates. The conclusions are based on monoculture growth under saturating light and nutrient abundance, or on

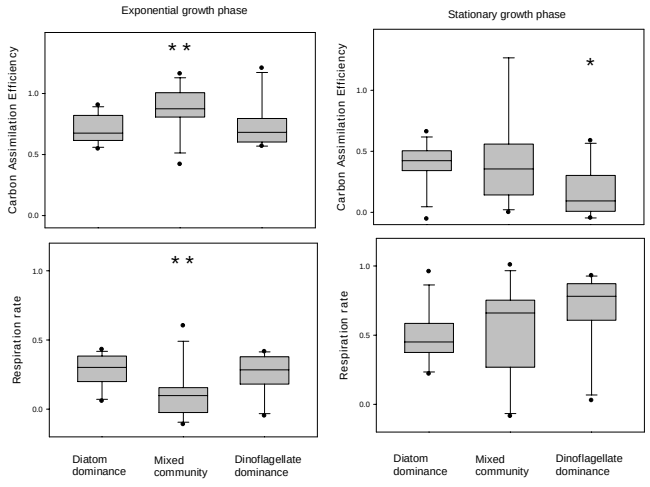


**Figure 5.** Carbon budget parameters: carbon assimilation efficiency and respiration, during exponential and stationary growth. The phytoplankton community was divided into three categories: diatom dominance (> 80 %), mixed community (20–70 % dinoflagellates), and dinoflagellate dominance (> 70 %). The rationale behind setting the group boundaries was based upon the apparent difference in species evenness (Fig. 1) between these groups. The stars indicate statistically significant differences ($\alpha = 0.05$) compared to one (*) or two (**) other groups; details can be found in Table 4.

continuous monocultures with established light or nutrient limitation, with the implicit or explicit assumption that the empirically derived traits can be utilized in modeling the performance of natural planktonic populations or communities (Cloern et al., 1995; Sarthou et al., 2005). Other angles to the phylogenetic–metabolic differences have been to address the evolutionary inheritance of elemental stoichiometry between phyla and superfamilies (Quigg et al., 2003), or to mechanistically model the stoichiometry of the nested biochemical processes underlying primary production of unicellular algae (Geider et al., 1998; Falkowski, 2000; Pahlow, 2005).

Our experiment series departs from these approaches by empirically studying the carbon flow and community stoichiometry over the full duration of natural, mixed community spring bloom events. During a multispecies bloom, the abiotic conditions and species interactions go through a continuous transformation, inducing transitory physiological acclimation responses and changes in competitive advantage between species. This seriously complicates prediction of bloom development with species-specific properties originating from growth in controlled, artificial monoculture conditions (Sathyendranath et al., 2009; Mateus et al., 2012). We used standardized, representative environmental conditions (light, temperature, nutrient supplies) and exclusion of advective and sedimentation flows to specifically address the net effects of variable diatom-to-dinoflagellate proportions of the bloom community on modification of coastal biogeochemistry.

Our experimental setup eliminated sinking losses that affect the overall bloom dynamics in open natural systems. Diatoms, in particular, are known to aggregate and sink efficiently out of the photic layer after bloom culmination (Kiørboe et al., 1990; Underwood et al., 2004). Our results therefore represent an upper limit for bloom C drawdown. However, the stoichiometric differences between different communities evolved fast after the bloom peak, and the variable physical forcing in coastal seas include changes in mixing of the surface layer, resuspension, and lateral transport, which counteract permanent sedimentation of fresh biogenic material, prolonging the stationary phase of bloom communities. This increases the heterotrophic remineralization in the water column.

### 4.2 Dominance patterns in experimental communities

The five initial communities represented the natural variability of phytoplankton in the respective years, as mesocosm communities developed from natural inocula. Interannual variability in community composition was considerable: years of dinoflagellate dominance alternated with years of diatom dominance or evenly mixed communities. The experimental treatments of light, nutrient supplies, and community structure amplified or further diversified the dominance patterns of the natural inoculum communities. This provided a wide range of dominance conditions in the altogether 36 mesocosms over multiweek bloom events, thus representing an ideal seminatural experimental system for community-level comparisons.

In the coastal study area, pre-bloom and bloom period weather patterns have been found to be significantly related to high dinoflagellate proportions during spring (Klais et al., 2013). Klais et al. (2013) reported that mild winters with thin ice cover and more storms favored dinoflagellates, suggesting that changing climate conditions are likely to drive the increasing frequency of coastal dinoflagellate-dominated spring blooms. Recent biodiversity shifts in offshore phytoplankton communities have been repeatedly linked to changing climate conditions (Reid et al., 1998; Hinder et al., 2012), modifying hydrographic properties of the water column, and thus selecting for specifically adapted taxonomic groups, most notably dinoflagellates (Hallegraeff, 2010).

While diatom dominance was in most cases caused by several co-occurring diatom species, the dinoflagellate blooms in the mesocosms consisted of a single species – *Biecheleria baltica* (formerly known as *Woloszynskia halophila*) or *Peridiniella catenata*. This seems to be a general phenomenon in a wide range of marine habitats: diatoms behave as guild members sharing the habitat, whereas dinoflagellates usually follow a taxonomical hierarchical pathway towards domination of one species (Smayda and Reynolds, 2001). Diatoms are, in general, tolerant to habitat diversity and are adapted to habitats with several ecological niches, whereas dinoflagellates often are habitat specialists where typically

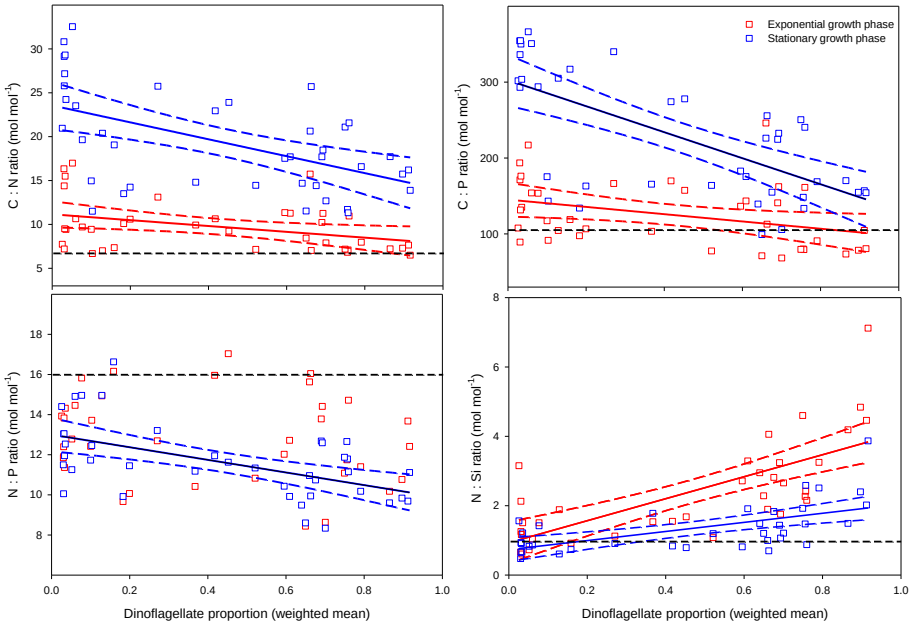


**Figure 6.** The particulate C : N, C : P, N : P, and N : Si ratios plotted against the weighted mean of dinoflagellate proportion during exponential (primary production peak) and stationary growth phase (end of experiment). The dashed horizontal line represent the Redfield–Brzezinski ratio (molar ratio); the red and blue line represents statistically significant linear regression of exponential and stationary growth phase data. Regression coefficients for the C : N ratio were slope $= -3.3$, $R^2 = 0.14$, and $p = 0.02$ and slope $= -9.6$, $R^2 = 0.29$, and $p = 0.0004$ for exponential and stationary growth phase, respectively. For the C : P ratio they were slope $= -48.0$, $R^2 = 0.13$, and $p = 0.03$ and slope $= -171.4$, $R^2 = 0.45$, and $p < 0.001$ for exponential and stationary growth phase, respectively. For N : P ratio, the linear regression for exponential growth phase was not significant ($p = 0.23$); the regression coefficients for stationary growth phase were slope $= -3.15$, $R^2 = 0.31$, and $p = 0.0002$. For the N : Si ratio they were: slope $= 3.06$; $R^2 = 0.51$; $p < 0.0001$ and slope $= 1.31$; $R^2 = 0.36$ and $p = 0.0001$ for exponential and stationary growth phase respectively.

the best-adapted species outcompete the rest (Smayda and Reynolds, 2001).

In dinoflagellate-dominated blooms, the respective species already constituted a major fraction of the initial community, by far outnumbering any other phytoplankton species, and were thus able to maintain dominance under several experimental treatments despite their relatively low species-specific growth rates (Kremp et al., 2008). Dinoflagellates have been shown to possess compensatory strategies to compete with fast-growing phytoplankton groups, such as allelopathy, mixotrophy, and internal nutrient storages (Legrand and Carlsson, 1998; Collos et al., 2004; Tillmann et al., 2008). *B. baltica* has recently been confirmed to effectively suppress growth of co-occurring diatoms by excretion of allelochemicals (Suikkanen et al., 2011), and utilization of residual P has been suggested to facilitate sustained growth of *B.baltica* in the 2004 mesocosms (Kremp et al., 2008).

### 4.3 Carbon production and losses during developing and late bloom stages

There were no significant differences between communities of diatom or dinoflagellate dominance in carbon-based growth rates ($\mu_{POC}$ or $\mu_{TGP}$) during the exponential bloom phase. This is somewhat counterintuitive, taking into account the general conclusions from monoculture studies and previous evidence that Baltic Sea dinoflagellates exhibit lower growth rates in mixed communities than the competing diatoms (Kremp et al., 2008). It should be noted that the carbon budgets are cumulative for the whole exponential phase, including also the variable delay periods from the experiment onset. Also, we are dealing with natural, mixed communities even in both "dominance" categories. Despite the differences in instantaneous growth rates between individual diatom and dinoflagellate species, the varying mixed communities thus performed production-wise comparably during the bloom accumulation phase.

Growth rates based on increase in Chl *a* were higher than carbon-based growth rates when diatoms were dominating. The faster accumulation of Chl *a* than carbon, on a community scale, could be caused by rapid synthesis of Chl *a* in diatoms based on reserve storage (Ross and Geider, 2009). This was supported by the difference in C : Chl *a* ratio between diatom- and dinoflagellate-dominated communities (Fig. 3). During diatom dominance, the C : Chl *a* ratio was rapidly decreasing during exponential growth phase, reflecting the difference in $\mu_{POC}$ and $\mu_{Chl\ a}$. The Chl *a*-based measurements overestimated the production rate under diatom dominance,

**Table 4.** Tukey's post hoc tests of carbon parameters during stationary growth phase. Only the statistically significant parameters from Table 2 were tested: particular organic carbon (POC), dissolved organic carbon (DOC), total gross production (TGP), and carbon assimilation efficiency (CAE). The phytoplankton community was categorized according to diatom dominance (diatoms), mixed community (mixed) and dinoflagellate dominance (dinoflagellates). The stars (*) indicate statistically significant differences ($\alpha = 0.05$).

| POC | Diff | St diff | $p$ value |
|---|---|---|---|
| Mixed vs. diatoms | 11.071 | 3.240 | 0.007* |
| Mixed vs. dinoflagellates | 4.029 | 1.120 | 0.509 |
| Dinoflagellates vs. diatoms | 15.100 | 4.060 | $< 0.001$* |
| DOC | | | |
| Mixed vs. diatoms | 11.464 | 3.094 | 0.011* |
| Mixed vs. dinoflagellates | 1.414 | 0.363 | 0.930 |
| Dinoflagellates vs. diatoms | 10.050 | 2.492 | 0.046* |
| TGP | | | |
| Mixed vs. diatoms | 12.381 | 3.416 | 0.005* |
| Mixed vs. dinoflagellates | 2.114 | 0.554 | 0.845 |
| Dinoflagellates vs. diatoms | 10.267 | 2.603 | 0.036* |
| CAE | | | |
| Mixed vs. diatoms | 2.512 | 0.654 | 0.791 |
| Mixed vs. dinoflagellates | 8.671 | 2.145 | 0.096 |
| Dinoflagellates vs. diatoms | 11.183 | 2.675 | 0.030* |

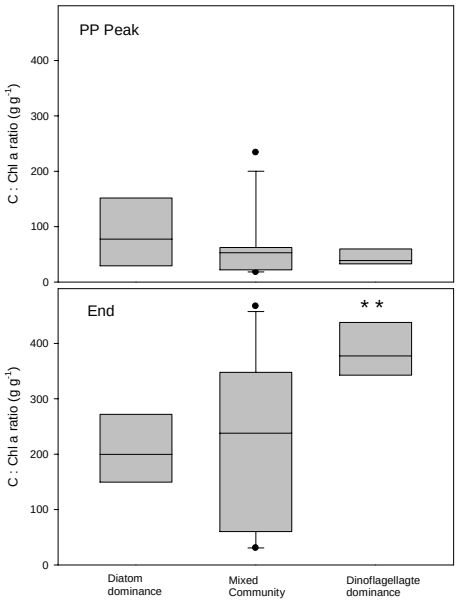


**Figure 7.** The C : Chl $a$ ratio at the primary production peak (PP) and at the end of the experiment (end). The phytoplankton community was divided into three categories: diatom dominance (> 80 %), mixed community (20–70 % dinoflagellates), and dinoflagellate dominance (> 70 %). The rationale behind setting the group boundaries was based upon the apparent difference in species evenness (Fig. 2).

and the results emphasize the importance of considering the currency of planktonic production measurements in large-scale estimates of aquatic primary production.

Our data showed that assimilation efficiency was highest in mixed communities, compared to either diatom or dinoflagellate dominance. This is in line with recent studies on the effects of biodiversity on community functioning, indicating that more diverse communities support higher resource use efficiency and productivity (Ptacnik et al., 2008; Worm et al., 2006; Stockenreiter et al., 2013; Striebel et al., 2009). Different species have different environmental requirements, occupying different niches in the ecosystem. With increased diversity, the probability of occupying more of the total niche space increases, leading to better utilization of resources.

The net metabolic differences within variable community dominance manifested themselves only after the exponential growth phase, when nutrients were effectively incorporated to biomass and loss processes became prominent. Net growth of primary producers is regulated by the balance of production and loss processes, such as respiration, excretion, sedimentation, and grazing. Sedimentation losses were eliminated in our experimental setup. Grazing effects were assumed to be minor because there are no overwintering populations of large copepods in the Baltic Sea, our experiments started with 200 µm pre-screening, and the grazing pressure by other heterotrophs on the large-celled (mostly > 20 µm) spring bloom diatoms or dinoflagellates is negligible (Lignell et al., 1993). The main loss pathways are therefore respiration and excretion of dissolved organic matter. The latter evidently possess high carbon-to-nutrient ratios, as particulate nutrient fractions remained relatively stable once inorganic nutrient pools were depleted during the exponential growth phase.

There was no statistically significant difference between respiration rates of communities dominated by diatoms or dinoflagellates. In monocultures, dinoflagellates have generally higher respiration ratio than diatoms (Spilling and Markager, 2008; Falkowski and Owens, 1978), but our experiments with natural mixed communities did not reproduce this difference reliably. During the exponential phase, respiration ratios were equal, whereas for the stationary stage high variability in the generally high respiration ratios of dinoflagellate-dominated communities (median 78 %) failed to yield significance for the apparent difference to diatom dominance. However, significantly lower assimilation efficiencies of dinoflagellate-dominated communities (median 10 %) were clearly driven by respiration, not by DOC release (Fig. 5).

Especially in diatom-dominated communities, POC continued to increase significantly after the primary production peak, and the communities kept fixing $^{14}CO_2$, as indicated

by the modeled carbon accumulation and relatively low (median 45 %) respiration ratios. Concomitant late bloom DOC release in diatom-dominated communities increased significantly over other communities, as well. The results from our natural diatom-dominated communities reproduced the early observations obtained with diatom batch monocultures by Goldman et al. (1992), who pointed out that the conventional new production concept, based on Redfield ratios (Dugdale and Goering, 1967), neglects the "excess" carbon fixation, due to uncoupling between photosynthesis and nutrient acquisition.

Our results showed that the post-peak bloom DOC accumulation was an order of magnitude lower than the parallel POC increase in diatom-dominated communities (note *y* axis scales in Fig. 1). DOC is by definition a pragmatic concept (organic carbon passing a glass-fiber filter with a nominal 0.7 µm porosity). Diatoms are known to excrete C-rich organic compounds of variable molecular weight as a means to dissipate harvested light energy, once biomass synthesis becomes limited by nutrient deficiency (Kiørboe et al., 1990; Underwood et al., 2004). It is likely that the colloidal and mucoid DOC fractions were progressively trapped on POC filters during the late bloom stages – potentially affecting, e.g., C : Chl *a* and $\mu$POC – when coagulation and aggregation of detrital matter with the continuum of "dissolved" organic carbon continued in the absence of sedimentation flows. Additionally, any labile DOC excreted was probably quickly utilized by bacteria and did not add to the measured DOC pool.

The overall conclusion of the C budgets for different communities is that, during the buildup of the bloom, differences between varying community dominance were far smaller than anticipated from monoculture studies. With regard to inorganic nutrient drawdown, exponential biomass development, and assimilation efficiency, diatoms and dinoflagellates acted to a large extent as functional surrogates. Major differences evolved only after the bloom culmination (coinciding with the depletion of inorganic nutrient pools and primary productivity peak), with significant consequences for carbon sequestration, C : N : P stoichiometry of spring bloom material flows, and the carbon-to-chlorophyll ratio of the communities.

### 4.4 Effects of community composition on nutrient stoichiometry and C drawdown during bloom events

The stationary phase of diatom-dominated communities strongly influenced the stoichiometry of seston, by doubling (112 % increase) the C content from the exponential phase compared both to N and P, and 1.6 times higher compared to stationary phase dinoflagellate dominance (Fig. 6). The net effect was therefore a 3.6-fold enhanced $CO_2$ sequestration to that expected from the Redfield ratio. Even dinoflagellate-dominated communities exhibited corresponding $CO_2$ drawdown enhancement to POC in the stationary phase, but at a significantly lower level (1.7-fold higher than the C : N, Redfield prediction). Carbon assimilation efficiencies in late bloom stages were very low for dinoflagellate-dominated communities due to high respiration rates, therefore preventing significant accumulation of organic C despite ongoing $^{14}C$ fixation. Dinoflagellate communities had a lower N : P ratio than diatom communities in stationary growth phase. Dinoflagellates have a high uptake affinity for P and keep assimilating it after growth stops (Kremp et al. 2008) probably due to their large genome, of which P is an essential component. The N : Si ratio of the seston was, as expected, affected by the dominance pattern (up to 4-fold difference) as only the diatoms are utilizing silicate. The fact that the DSi addition had little to no effect on the outcome suggests that the initial DSi concentration was sufficient for the diatom community and did not affect the competition with dinoflagellates.

The excess carbon fixation noted in a stationary diatom batch culture (Goldman et al., 1992) was supported in field conditions by chemical proxies and discussed within the "biological pump" framework, as a vehicle transporting more $CO_2$-derived carbon from the atmosphere to the oceans than expected from nutrient availability and fixed Redfield ratios (Sambrotto et al., 1993). Engel et al. (2002) showed that a major component of the emerging high POC : PON ratios in an experimentally induced natural diatom community bloom was aggregation of "marine snow" (72 % more dissolved inorganic carbon fixation than inferred from nitrate supply and Redfield stoichiometry), following a large late-bloom flow of carbon into transparent exopolymer particles (TEPs). Schartau et al. (2007) modeled this "carbon overconsumption" flux based on the experimental results, and addressed 30 % of the POC increase to TEP formation.

Our results clearly support the "overconsumption" carbon flow pattern for a natural diatom-dominated bloom presented by Engel et al. (2002) and modeled by Schartau et al. (2007), but the difference of our results to Redfield-based estimates was even higher. The diatom community of Engel et al. (2002) exhibited close-to-Redfield stoichiometry during the bloom accumulation phase, while our diatom-dominated exponential phase communities showed seston C : N and C : P ratios almost double and triple the corresponding Redfield ratios, respectively. In the stationary phase, our strongest diatom-dominated communities had up to 3.6 times higher seston C : N content (regression in Fig. 6) than anticipated from Redfield ratios, as compared to 72 % by Engel et al. (2002).

Estimates of offshore carbon overconsumption in the field, based on integrative geochemical approaches to in situ variations of chemical species, were reported up to 300 % in the "Vanishing in Bermuda" debate and Joint Global Ocean Flux Study (Toggweiler, 1994; Michaels et al., 1994; Marchal et al., 1996), soon after the experimental observations of Goldman et al. (1992), who found C : N ratio enhancement of ca. 200 % in late-phase diatom cultures. Our N-based

"C overconsumption" for coastal, diatom-dominated natural community bloom events (up to 3.6 times higher) therefore not only support but also expand these observations, in terms of (a) the observed ranges of C overconsumption, (b) direct measurements of bloom events by natural mixed phytoplankton communities, and (c) geographically covering a coastal regime. Most importantly, however, we also show that the bloom community composition significantly affects the level of C overconsumption. Dinoflagellate-dominated communities showed a similar pattern of increasing carbon-to-nutrient ratios of seston from exponential to stationary phases, but with clearly smaller departures from the Redfield stoichiometry than under diatom dominance (1.7 times higher than Redfield C : N).

### 4.5 Carbon-to-chlorophyll ratio and community composition

A stoichiometric ratio of particular interest for large-scale estimates of aquatic primary production, either for geographically defined provinces or globally, is the carbon-to-chlorophyll ratio. Implementing numerical models of primary productivity requires either direct carbon-based phytoplankton observations or incorporation of fixed (Cloern et al., 1995) or dynamic C : Chl *a* ratios (Taylor et al., 1997). Phytoplankton C is notoriously difficult to separate from seston C, and no methods for direct measurements in the field are available. Most available spatially extensive observations originate from satellite remote sensing of chlorophyll, which requires bridging to carbon-based models (Behrenfeld and Falkowski, 1997). Currently, advanced oceanic biogeochemical models include dynamic C : Chl *a* ratios with photoacclimation parameterization, the most common of which is the Geider et al. (1998) model or its derivatives (Sathyendranath et al., 2009; Baird et al., 2013).

Carbon-to-chlorophyll ratios are known to be highly variable both in monocultures and in nature (Taylor et al., 1997; Chan, 1980), and the photoacclimation models are generally parameterized with monoculture responses to controlled laboratory conditions, most often highly departing from any set of natural conditions. Major uncertainty is introduced when laboratory models are translated for application to field models if the sources of C : Chl *a* variability are not sufficiently understood and accounted for (Sathyendranath et al., 2009). These sources are normally addressed as responses of cultured algae to light and nutrient availability, which certainly are the key drivers for photosynthesis and the maintenance of the photosynthetic machinery, including cellular quotas for C, N, and P. However, species- or group-specific differences in these responses have rarely been incorporated, and the ability of photoacclimation models to cope with functionally different phytoplankton groups and non-steady-state natural conditions is a major current challenge for variable stoichiometry models (De La Rocha et al., 2010).

Our results showed that both the growth stage of a bloom and the species dominance patterns strongly affected the community C : Chl *a* ratios. The lowest ratios (30 to 80; g : g) were encountered during the primary productivity and Chl *a* peak phases, when the community composition had a minor effect. During senescent bloom stages, diatom-dominated communities developed 4-fold C : Chl *a* ratios (median 200), whereas dinoflagellate-dominated communities showed median values of ca. 400, in similar irradiance, temperature, and nutrient-depleted conditions. These transient, order-of-magnitude changes within a few weeks during bloom events, with a strong component of species composition, present so-far-overlooked challenges for models of phytoplankton acclimation and geographically extensive production estimates based on satellite remote sensing.

An interesting difference between the diatoms and dinoflagellates, dominating the spring bloom in the Baltic Sea, is their different response to the onset of inorganic N depletion. Diatoms continued to run photosynthesis building up the internal C storage, and also releasing C as DOC, probably as a way of dissipating excess light energy (Myklestad et al., 1989; Staats et al., 2000). Dinoflagellates, in contrast, seem to shut down the photosynthetic machinery earlier as a way to acclimate to a condition with reduced need for inorganic carbon fixation. The observed increase in C : Chl *a* in the two groups could have different causes, for the diatoms primarily an increase in POC, while for the dinoflagellates the decrease in Chl *a* was relatively more important.

### 4.6 Community change in changing climate

Competition between cold-water dinoflagellates and diatoms represents an important aspect of community change, especially in changing climatic conditions of coastal temperate and Arctic environments. Other well-documented, increasing dinoflagellate occurrences amidst diatom dominance that suggest climatic connotations are warm-water harmful algal blooms (Hallegraeff et al. 2010), while in several marine habitats, prymnesiophytes (especially *Emiliania huxleyi* and *Phaeocystis*; Breton et al., 2006) are the main competitors for diatoms. Our results indicate that such variation in phytoplankton community dominance patterns have potentially significant consequences for marine biogeochemical cycles that need to be addressed, as ca. half of global primary production is attributed to marine systems, with phytoplankton as the main component (Field et al., 1998).

Application of either fixed Redfield stoichiometry, or uniform "phytoplankton" stoichiometry, can lead to several-fold errors or uncertainties in estimates for $CO_2$ sequestration, especially during temperate and Arctic spring blooms. In dynamic natural bloom conditions, distinguishing between community composition and physiological acclimation during varying bloom stages, as sources of variation in seston stoichiometry, therefore remains a major challenge for trait-based phytoplankton ecology.

Marine biota are often regarded and studied as mere passive objects of climate change, and their responses to changes in, e.g., temperature, acidification, stratification, and light climate of the mixed surface layer are accordingly actively studied. It appears essential to focus equally on the active role of phytoplankton in climate change: how marine carbon sequestration and interconnected biogeochemical cycles are directly modified by community change. Incorporating functional diversity and stoichiometric flexibility of primary producers into marine biogeochemical models is therefore a pending task for climate change research. An obvious parallel challenge for geographically extensive estimates of marine primary production is enhanced taxonomical resolution of remote sensing technologies, to cope with the ongoing large-scale community change and its biogeochemical consequences.

*Acknowledgements.* This study was funded by the Academy of Finland (decision no. 111336 & 263862); funding was also provided by the Walter and Andrée de Nottbeck Foundation (KS) and Estonian Research Council grant PUT39 (K. Olli and R. Klais). We would like to thank all the staff at Tvärminne Zoological Station (Univ. Helsinki) for all technical assistance and Päivi Hakanen for her assistance in the microscopy work.

Edited by: M. Dai

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